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Ken-ich Ito · Akira Isogai · Fumihiko Onabe

Retention behavior of size and aluminum components on handsheets in rosin-ester size/alum systems*

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Abstract Anionic emulsion sizes consisting of rosin triglyceride esters and partly fortified rosin acids (i.e., rosin-ester sizes), have recently been used as internal sizes for alkaline papermaking. In this study, handsheets were prepared from pulp suspensions with alum and a rosin-ester size under various conditions, and sizing degree and size and aluminum contents of the handsheets were determined. Aluminum compounds originating from alum added to the pulp suspensions behave as retention aids of the rosin-ester size even in alkaline papermaking under limited conditions. Carboxyl groups in pulp are the primary retention sites of aluminum compounds in pulp suspensions. They form cationic sites on pulp fibers, and thus the anionic size emulsion particles are adsorbed on pulp fibers by electrostatic interactions. However, the cationic charges of aluminum compounds on pulp fibers decrease and finally disappear completely with the lapse of time after the alum addition by forming ionic bonds between the cationic sites and OH^- ions. Thus, pH values of the pulp suspensions and timing of the size addition strongly influence the retention values of the rosin-ester size and the resultant sizing features.

Key words Rosin-ester size · Aluminum sulfate · Retention · Alkaline sizing · Paper

K. Ito
Laboratory of Japan PMC Co. Ltd., Ichihara 290-0067, Japan

A. Isogai (✉) · F. Onabe
Graduate School of Agricultural and Life Science, The University of Tokyo, Tokyo 113-8657, Japan
Tel.+81-3-3812-2111 (ext. 5271); Fax +81-3-5684-0299
e-mail: aisogai@hongo.ecc.u-tokyo.ac.jp

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Introduction

Alkylketene dimers (AKD) and alkenylsuccinic anhydrides (ASA) have been used as typical internal sizes for alkaline papermaking, although these so-called reactive sizes sometimes lead to problems in paper quality, the runnability of papermaking, or both. The rosin-ester sizes have recently been developed as new internal sizes for alkaline papermaking in these circumstances.[1–3] General rosin-ester sizes in commercial products are anionic emulsions consisting of rosin triglyceride esters, partly fortified rosin acids and an anionic polymer surfactant. In the practical rosin-ester sizing, alum and cationic polymers are used as additives to pulp suspensions at pH 7–8 containing $CaCO_3$ filler. In acid papermaking with rosin sizes, aluminum ions originating from alum and carboxyl groups in pulp form cationic structures such as Pulp-$COOAl^{2+}$ and Pulp-$COOAl(OH)^+$ in pulp suspensions. Anionic sites of rosin size emulsion particles are therefore adsorbed on pulp fibers by forming ionic bonds at the cationic sites.[4–7] It is known that alum loses its cationic charges to form nonionic $Al(OH)_3$ flocs under alkaline conditions, and the role of alum in the rosin-ester sizing has not yet been clarified.[8–14]

Therefore, to make clear the roles of alum in rosin-ester sizing, handsheets were prepared under various conditions, and sizing behavior of the handsheets was studied in terms of size and aluminum contents.

Materials and methods

Materials

A commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. Carboxyl group-blocked pulp was prepared from the above beaten pulp by methylamidation with water-soluble carbodiimide and methylamine at pH 4.75.[5,15,16] Carboxyl contents measured by the TAPPI test method[17] were 60 and 2 μEq/g for the original and carboxyl group-blocked pulps, respectively. The rosin-ester size used was prepared in the laboratory of the first author; an anionic emulsion of 50% solid content consisting of size components (rosin triglyceride esters and partly fortified rosin acids with 1:1 by weight) and an emulsion stabilizer (polyacrylic acid sodium salt-polystyrene type copolymer). Aluminum sulfate of pure grade (Wako Chemicals, Japan) and a $CaCO_3$ filler were used as additives.

Handsheet production

In general procedure, to a 0.15% pulp suspension at 40°C, whose pH was adjusted to 8 with a diluted NaOH solution, certain amounts of $Al_2(SO_4)_3$ and the rosin-ester size were added, in this order, with continuous stirring. The interval between the $Al_2(SO_4)_3$ and size additions was usually set at 10s. The final pH values of the pulp suspensions became 0.2–1.6 lower than the initial ones, depending on the amount of $Al_2(SO_4)_3$ added. After being stirred for 30s, the pulp suspensions were subjected to prepare handsheets with a basis weight of 60g/m^2 according to the TAPPI test method[18] by diluting the pulp suspension with tap water at 20°C and pH 6.9. The wet-pressed handsheets were dried at 20°C and 65% relative humidity for more than 1 day, and then the handsheets were cured at 105°C for 20min.

Analyses

Sizing degrees of the handsheets were evaluated by the Stöckigt method.[19] A scanning electron microscope (SEM) (S-4000; Hitachi, Japan) equipped with an energy dispersive X-ray analyzer (EDXA) (EMAX-5770X; Horiba, Japan) and an X-ray fluorescence analyzer were used for determining aluminum contents in the handsheets.[14] Measuring conditions were the same as those reported in a previous paper.[14] Size contents in the handsheets were determined by pyrolysis-gas chromatography (PY-GC) using the on-line methylation technique with a 25% tetramethylammonium hydroxide/methanol solution.[1,3,20]

Results and discussion

Rosin-ester sizing of pulp suspensions containing $CaCO_3$ filler

Figure 1 shows sizing degrees of the handsheets prepared from pulp suspensions containing a $CaCO_3$ filler at 40°C by the addition of alum and the rosin-ester size. When 2% (on dry weight of pulp) $Al_2(SO_4)_3$ was added to the pulp suspensions, the handsheets had sizing features at more than 0.5% addition levels of the rosin-ester size, although their sizing degrees were lower than 10s even at the 2% addition level. No or quite low sizing features appeared on the handsheets when 1% $Al_2(SO_4)_3$ was added. Size and aluminum contents in the handsheets are illustrated in Fig. 2. All size components, such as rosin-triglycerides, rosin acids, and rosinate salts, can be converted to rosin acid methyl esters by the online methylation with tetramethylammonium hydroxide during the pyrolysis.[1,3] Size contents increased with increasing addition levels of the rosin-ester size. Aluminum contents slightly decreased with the rosin-ester size additions for both the 1% and 2% $Al_2(SO_4)_3$ additions. Thus, the

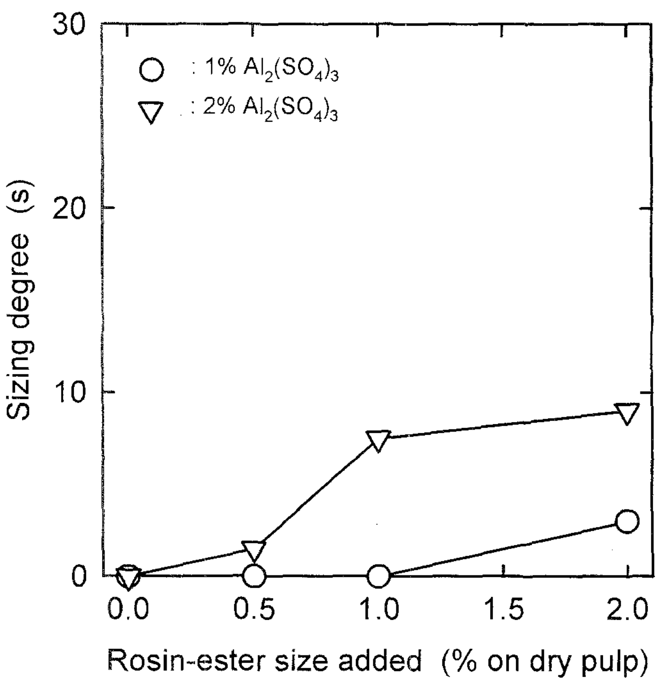

Fig. 1. Sizing degree of handsheets prepared from pulp suspensions containing 20% (on dry weight of pulp) $CaCO_3$ filler in the rosin-ester size/alum sizing

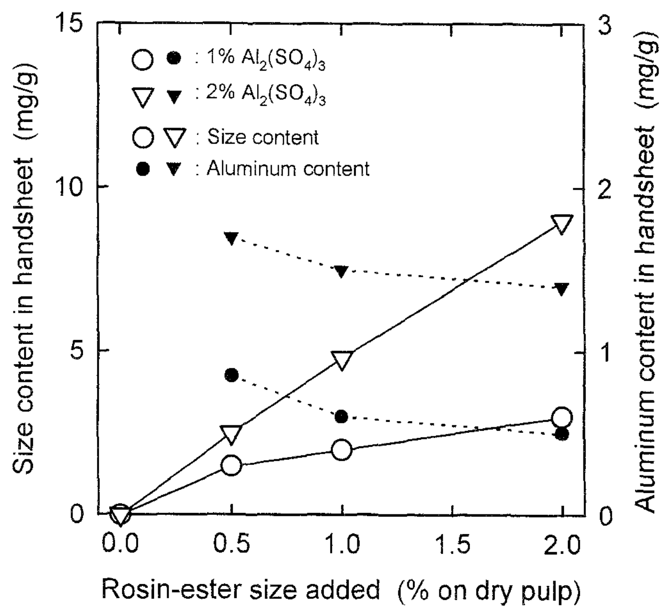

Fig. 2. Size and aluminum contents in handsheets prepared from pulp suspensions containing 20% (on dry weight of pulp) $CaCO_3$ filler in the rosin-ester size/alum sizing

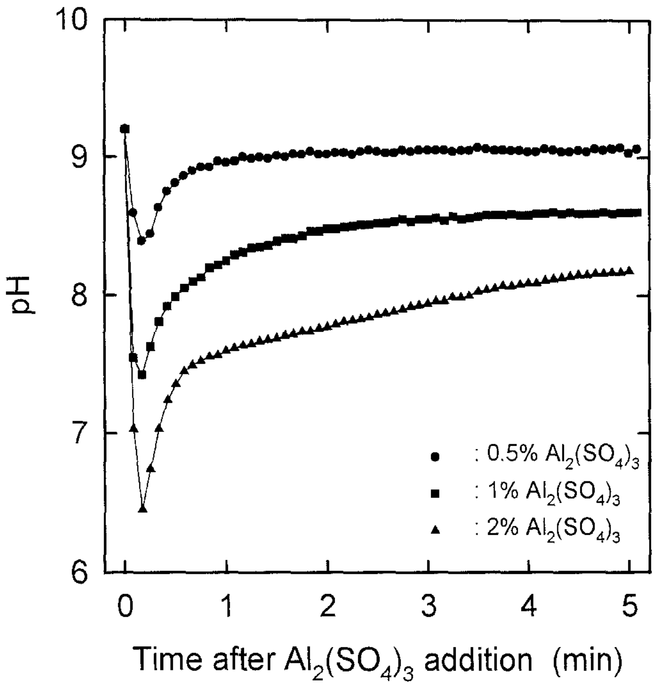

Fig. 3. Changes in pH of 0.15% pulp suspensions containing 20% (on dry weight of pulp) $CaCO_3$ filler by alum additions

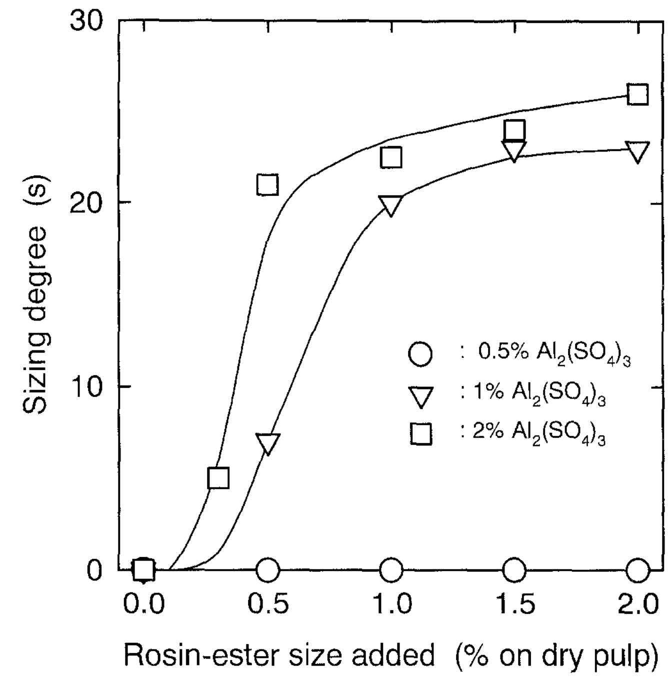

Fig. 4. Effect of level of rosin-ester size on sizing degree of handsheets prepared from pulp suspensions at an initial pH of 8

rosin-ester size can be retained in handsheets only by alum even in alkaline papermaking under limited conditions.

Figure 3 shows changes in pH of 0.15% pulp suspensions containing 20% (on dry weight of pulp) $CaCO_3$ after the alum additions. In these 0.5%, 1.0%, and 2.0% $Al_2(SO_4)_3$ additions, pH values rapidly dropped within 20s and then increased with time. Furthermore, alum had some buffering effects, and thus pH values did not reach the initial pH value of 9.2 even after 5 min of stirring the pulp suspension containing $CaCO_3$. It is well known that all aluminum components originating from alum turn to nonionic $Al(OH)_3$ in water at pH values of more than 5.5 under equilibrium conditions, and so any anionic compounds such as the rosin-ester size ought not to be retained in the handsheets. Nevertheless, alum could behave as a retention aid of the rosin-ester size in pulp suspensions even in the presence of the $CaCO_3$ filler. That is, a part of the aluminum components are adsorbed on pulp fibers in the pulp suspensions, maintaining their cationic charges to some extent, and so the anionic rosin-ester emulsion particles can be adsorbed on pulp fibers at these cationic sites by electrostatic interactions. Because the formation of ionic bonds between cationic aluminum compounds on pulp fibers and anionic size emulsion particles competes with that between cationic aluminum compounds and OH^- ions in the pulp suspensions, timing of the rosin-ester size addition must be significant for the size retention, as described later. In this experiment, the rosin-ester size was added to the pulp suspensions 10s after the alum addition. Therefore, the adsorption of aluminum components on pulp fibers and the adsorption of size emulsion particles on pulp fibers must have occurred around these lowest pH regions.

Effect of addition of alum and rosin-ester size

On the basis of the results obtained in the previous section, the handsheet-making was carried out for pulp suspensions whose initial pH was set at 8 with a diluted NaOH solution without using the $CaCO_3$ filler for convenience. The pH values of the pulp suspensions were shifted to 7.5–6.4, depending on the addition levels of alum; and they no longer increased with time. However, these shifted pH values were nearly equal to the lowest pH values observed in Fig. 3 at each level of $Al_2(SO_4)_3$. Then, to clarify interactions among pulp fibers, aluminum compounds, and rosin-ester size emulsion particles occurring around these lowest pH regions, pulp suspensions having an initial pH of 8 were used in this section.

Figure 4 shows the effect of the addition of the rosin-ester size on sizing degrees of the handsheets, and Fig. 5 illustrates the size and aluminum contents in the handsheets. Compared with Figs. 1 and 2, sizing degrees as well as size and aluminum contents were higher for the pulp suspensions without the $CaCO_3$ filler. The increase in pH values of pulp suspensions with time after the alum addition may have resulted in these lower sizing and retention values for the $CaCO_3$-containing pulp suspensions. When 0.5% (on dry weight of pulp) $Al_2(SO_4)_3$ was added, neither aluminum nor size component was retained at all in the handsheets. Probably, most aluminum components added to the pulp suspensions at the initial pH of 8 immediately form nonionic $Al(OH)_3$ by reacting with OH^- ions. On the other hand, at the 1% and 2% $Al_2(SO_4)_3$ additions, aluminum components were clearly retained in the handsheets, and their contents were constant to the levels of the rosin-

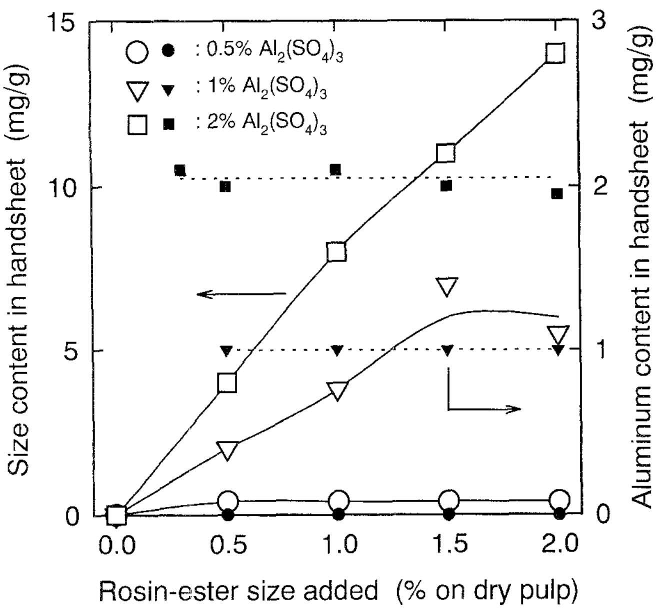

Fig. 5. Effect of level of rosin-ester size on size and aluminum content in handsheets prepared from pulp suspensions at an initial pH of 8

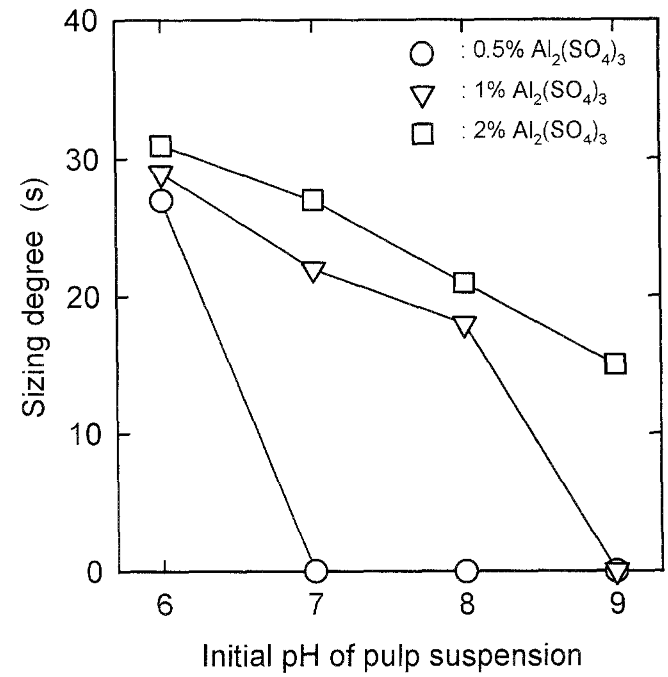

Fig. 6. Effect of initial pH of pulp suspensions on sizing degree of handsheets. Level of rosin-ester size: 1% on dry weight of pulp

ester size. Therefore, aluminum components other than nonionic $Al(OH)_3$ are mostly adsorbed on pulp fibers in the pulp suspensions and form cationic sites there. The anionic emulsion particles of the rosin-ester size can be thus adsorbed on the cationic sites of pulp fibers by electrostatic interactions.

Effect of initial pH of pulp suspensions

Figure 6 shows sizing degrees of the handsheets prepared from pulp suspensions, whose initial pH values were adjusted to 6, 7, 8, or 9 with a diluted NaOH solution; the corresponding size and aluminum contents are illustrated in Figs. 7 and 8, respectively. The 0.5% $Al_2(SO_4)_3$ addition to the pulp suspensions at pH 6 produced sizing degrees almost equal to those for the handsheets prepared with 1% and 2% $Al_2(SO_4)_3$ additions. Also the size contents were roughly equal among the handsheets prepared with 0.5%, 1.0%, and 2.0% $Al_2(SO_4)_3$ at an initial pH of 6. Thus, aluminum content of about 0.7 mg/g in the handsheets must be sufficient for retention of the anionic rosin-ester size emulsion particles, so long as the aluminum components maintain their cationic charges on pulp fibers under these weakly acidic conditions (Fig. 8). However, even though certain amounts of aluminum components are adsorbed on pulp fibers, their cationic charges must decrease with an increasing initial pH of the pulp suspensions or with increasing OH^- concentration. Furthermore, as shown in Fig. 8, no aluminum components were retained in the handsheets when they were prepared at the initial pH of 9 with the 1% $Al_2(SO_4)_3$ addition level, probably because of the formation of nonionic $Al(OH)_3$ for most aluminum components added.

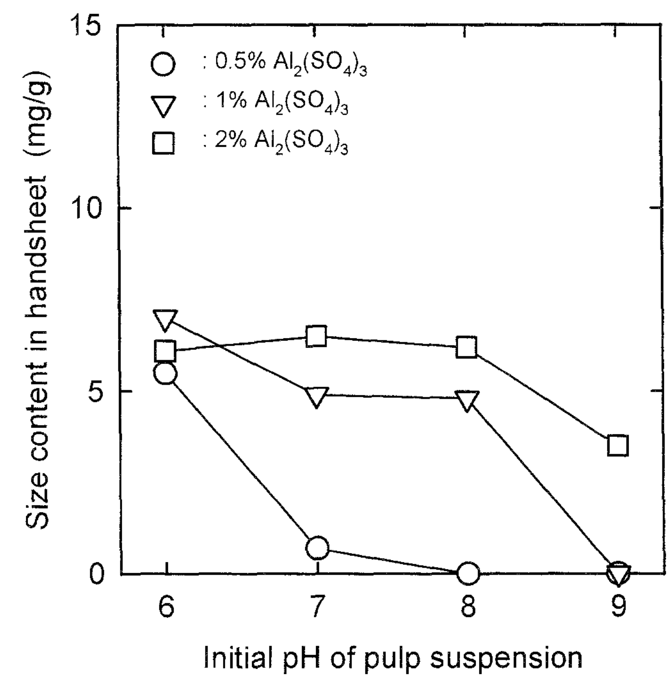

Fig. 7. Effect of initial pH of pulp suspensions on size content in handsheets. Level of rosin-ester size: 1% on dry weight of pulp

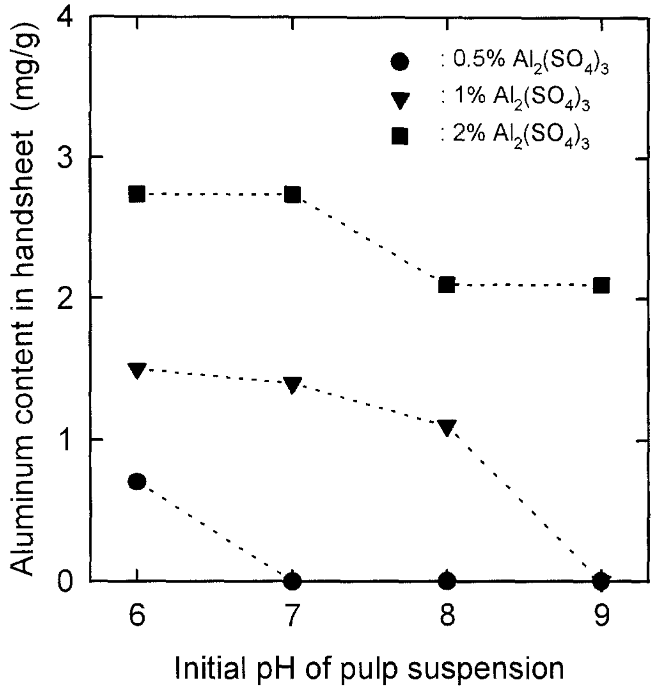

Fig. 8. Effect of initial pH of pulp suspensions on aluminum contents in handsheets. Level of rosin-ester size: 1% on dry weight of pulp

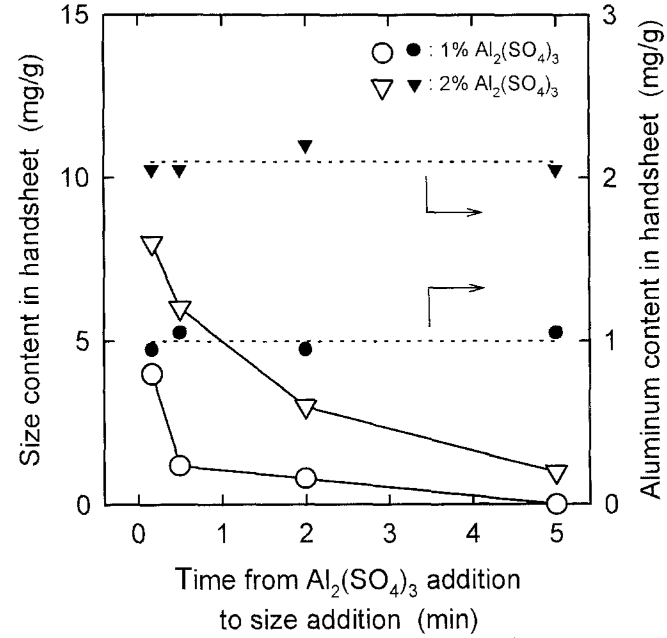

Fig. 10. Effect of stirring time of pulp suspensions between alum and rosin-ester size additions on size and aluminum contents in handsheets. Level of rosin-ester size: 1% on dry weight of pulp

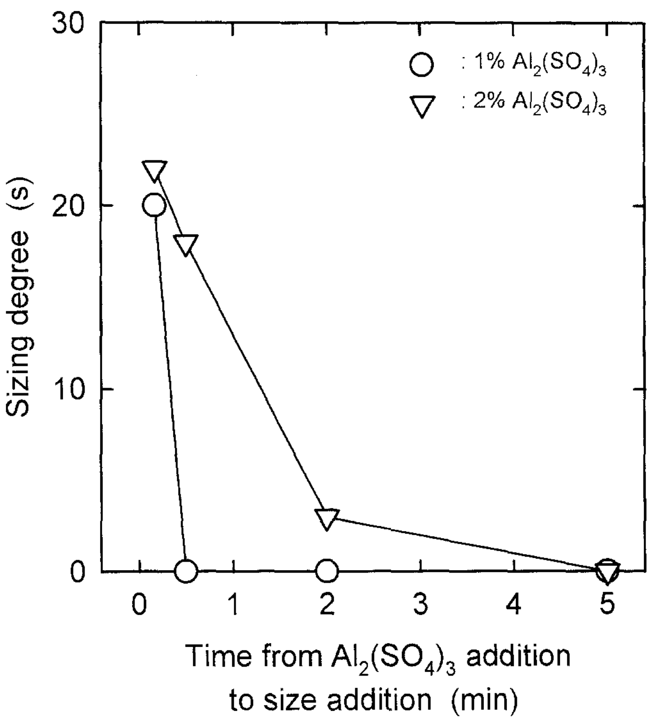

Fig. 9. Effect of stirring time of pulp suspensions between alum and rosin-ester size additions on sizing degree of handsheets. Level of rosin-ester size: 1% on dry weight of pulp

Therefore, retention of the rosin-ester size in the handsheets or interaction among pulp fibers, aluminum compounds originating from alum, and the anionic rosin-ester size emulsion particles in pulp suspensions under alkaline conditions is strongly influenced by ionic reactions between cationic aluminum compounds originating from alum and OH^- ions.

Effect of elapsed time between addition of alum and size

Figure 9 shows sizing degrees of the handsheets prepared with alum and the rosin-ester size, where the stirring time of the pulp suspensions between alum and size additions varied. The size and aluminum contents in the handsheets were illustrated in Fig. 10. Increasing the elapse of time after the alum addition drastically dropped sizing degrees of the handsheets. These sizing features corresponded well with size contents in the handsheets; retention values of the rosin-ester size decreased with increasing stirring time of the pulp suspensions after the alum addition. On the other hand, aluminum contents in the handsheets were constant to the stirring time of the pulp suspensions for both 1% and 2% $Al_2(SO_4)_3$ additions (Fig. 10). These results imply that the cationic charges formed on pulp fibers by aluminum compounds originating from alum decrease with increasing stirring time in the pulp suspensions. Before anionic sites of each size emulsion particle (i.e., dissociated carboxyl groups of the size emulsion stabilizers) are adsorbed on the cationic sites of aluminum compounds on pulp fibers, OH^- ions must react with the cationic sites to form nonionic hydroxide-type structures during the stirring of the pulp suspensions.[14]

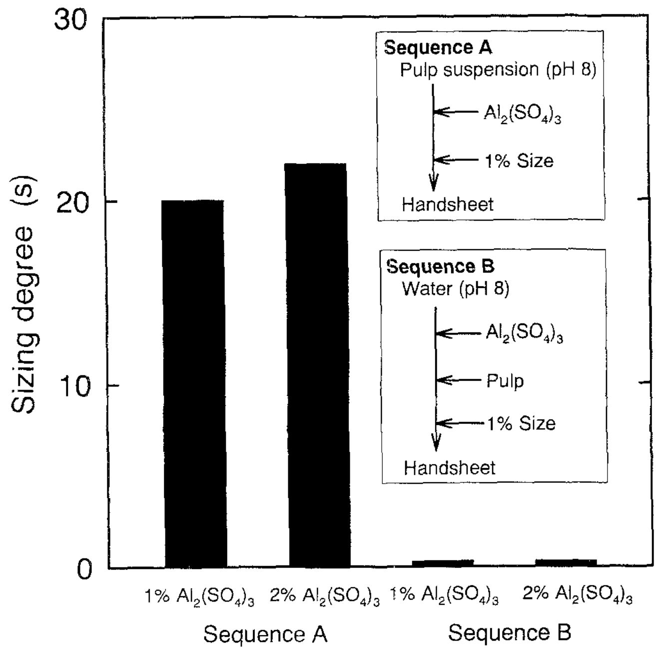

Fig. 11. Effect of addition sequence of alum and rosin-ester size on sizing degree of handsheets

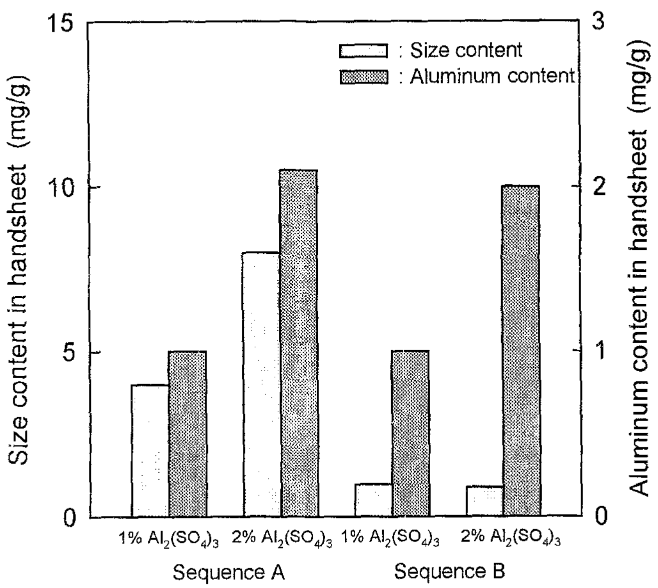

Fig. 12. Effect of addition sequence of alum and rosin-ester size on size and aluminum contents in handsheets

Effect of addition sequence of alum and rosin-ester size

Two addition sequences of pulp, alum, and the rosin-ester size were carried out during handsheet-making. Sizing degrees and size and aluminum contents of the handsheets are shown in Figs. 11 and 12. Expectedly, the sequence B in Fig. 11 gave no sizing features at all to the handsheets, and correspondingly their size contents were quite low, compared with those for the sequence A. However, aluminum contents in the handsheets were almost equal between sequences A and B for both 1% and 2% $Al_2(SO_4)_3$ addition levels. Therefore, aluminum compounds are adsorbed on pulp fibers in a similar manner for the two addition sequences A and B. However, the aluminum compounds on pulp fibers in sequence B must no longer have the capability to adsorb anionic size emulsion particles, because most cationic charges have been lost by the formation of ionic bonds between the cationic sites of aluminum compounds and OH^- ions.

Therefore, in the rosin-ester sizing using alum, adsorption of the size components on pulp fibers under alkaline conditions is explained in terms of competition reactions at the cationic sites of aluminum compounds on pulp fibers between anionic sites of each size emulsion particle and OH^- ions. Alum added to the pulp suspensions therefore behaves as a cationic retention aid even during alkaline papermaking under limited conditions. On the other hand, discussions on interactions between paper components in pulp suspensions under equilibrium conditions do not make any sense for explaining retention mechanisms of the rosin-ester size using alum in alkaline papermaking.

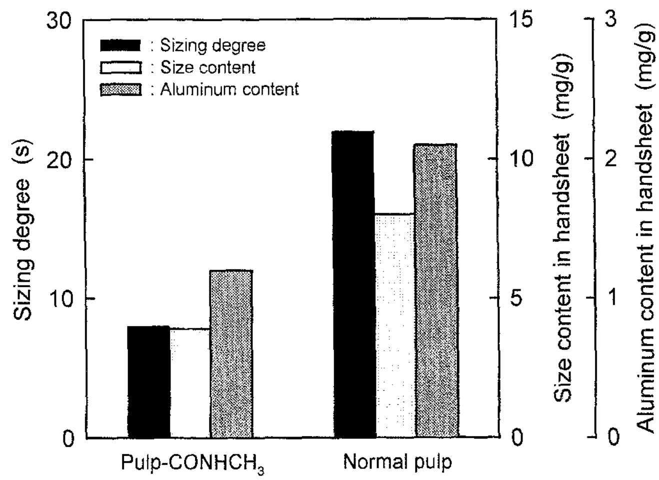

Fig. 13. Effect of blocking of carboxyl groups in pulp on sizing degree and size and aluminum contents of handsheets. Levels of $Al_2(SO_4)_3$ and rosin-esterer size: 1% and 2%, respectively, on dry weight of pulp

Effect of carboxyl groups in pulp

The effect of carboxyl groups in pulp on the rosin-ester sizing was studied using the carboxyl group-blocked pulp, Pulp-$CONHCH_3$ (Fig. 13). Sizing degrees of the handsheets prepared from this pulp were about one-third of those prepared from normal pulp. Correspondingly, the size and aluminum contents in the former handsheets decreased to about half of those for the latter handsheets. Therefore, more than half of the aluminum components retained in the handsheets prepared from normal pulp are explained in terms of the formation of ionic bonds between Pulp-COO^- and cationic aluminum compounds originating from alum added to the pulp suspensions. However, a part of cationic aluminum compounds can be retained in the handsheets without such electrostatic interactions. Because hydroxyl groups of cellulose have no electrostatic interactions with low-molecular-weight cationic aluminum ions,[21] these aluminum compounds may form cationic flocs, and they are adsorbed on pulp fibers by hydrogen bonding, van der Waals interactions, coordinate bond formation between pulp fibers and cationic aluminum flocs, or a combination of these actions. It is also possible in the case of handsheet-making using the COOH-blocked pulp that cationic aluminum compounds and anionic size emulsion particles form flocs by coagulation in the pulp suspensions because cationic aluminum compounds may preferably form ionic bonds with anionic sites of the size emulsion particles. If these flocs are formed, a part of them must be retained on the pulp fiber matrix by simple filtration effects during the drainage process of the handsheet-making. However, it can still be concluded on the basis of the results in Fig. 13 that, so long as normal kraft pulps are used, carboxyl groups in the pulp fibers play a significant role in effective retention of the anionic rosin-ester size emulsion particles when alum is used in alkaline papermaking.

Conclusions

Handsheets were prepared from pulp suspensions with alum and the rosin-ester size under various conditions, and the following conclusions were drawn based on the sizing behavior and the size and aluminum contents of the handsheets.

1. Aluminum sulfate behaves as retention aids of the anionic rosin-ester emulsion size even in alkaline papermaking under limited conditions.

2. Aluminum components originating from alum added to pulp suspensions are retained in the handsheets primarily by the formation of ionic bonds between Pulp-COO^- and cationic aluminum compounds in pulp suspensions.

3. On the other hand, a part of the aluminum compounds are retained in the handsheets by some effects other than the electrostatic interactions.

4. Because cationic sites of aluminum compounds on pulp fibers can react with both anionic sites of each size emulsion particle and OH^- ions competitively, pH values of the pulp suspensions strongly influence the retention values of the rosin-ester size and the resultant sizing behavior.

5. Especially, cationic charges of aluminum compounds on pulp fibers decrease with increasing time after the alum addition by reacting with OH^- ions. Finally, nonionic aluminum compounds are formed on pulp fibers, and they no longer have the capability to adsorb anionic size emulsion particles.

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